

PATENT SPECIFICATION

(11) 1 524 782

1 524 782

- (21) Application No. 2804/77 (22) Filed 24 Jan. 1977
(31) Convention Application No. 16
(32) Filed 24 Jan. 1976 in
(33) India (IN)
(44) Complete Specification published 13 Sept. 1978
(51) INT CL² C07C 69/66
(52) Index at acceptance
C2C 20Y 231 240 264 30Y 360 361 362 366 368 36Y 638 643 648
CV



(54) PRODUCTION OF ESTERTYPE POLYOLS

(71) We, THE INDIAN SPACE RESEARCH ORGANISATION, an Indian Company of Department of Space, 'F' Block, Cauvery Bhavan, District Office Road, Bangalore 560009, India, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with novel polyols and a process for producing such polyols.

Polyols or hydroxyl terminated polymers are the precursors of urethane polymers. Most of the commercial polyols are of polyether or polyester type. However, the polyether types have so far found wider applications and larger demand as compared to polyester type polyols in the urethane industry. Naturally occurring ester type polyols, like castor oil, have also been found suitable for various commercial applications. Castor oil and its derivatives have been used as polyols in three different ways: (a) unmodified castor oil as basic polyol (b) its transesterified product, and (c) esters of its fatty acids. The ester type polyols mentioned above could not lead on to wide and bulk applications in the urethane industry as any modification in chemical structures of the ester type polyols was aimed to meet only a specific end use.

There have previously been attempts to get polymers from fatty acids of castor oil for various applications. For example, according to US Patent No. 2,785,978 mixture of fatty acids of castor oil have been intramolecularly polymerised at 200° to 230°C in vacuum for 16 hours under nitrogen atmosphere and further the resulting estolides have been esterified with high molecular weight polyglycerol. These products have been reported to be useful in the preparation of water-in-oil emulsion and chocolate coating for ice-cream briquettes. Almost similar products have been produced in semi-liquid or pasty form as described in Dutch Patent No. 82,891 and they are used as stabilizers and emulsifying agents.

Ehrlich, A., M. K. Smith and T. C. Patton, (J. Am. Oil Chem. Sec. 36, 149 (1959)) have reported various ricinoleic acid and 12-hydroxystearic acid polyols for urethane foams and elastomer applications. These polyols are low molecular weight monoesters of ricinoleic acid and 12-hydroxystearic acid with various glycols, glycerol or pentaerythritol. Though the polyols thus prepared would have higher functionality and increased molecular weight to a limited degree, the concept of polymerising the fatty acids of castor oil and suitably modifying the same has not been cited. Low molecular weight monoesters of ricinoleic acid have also been reported by Baker Castor Oil Co., USA under the trade name of Polycin. [See Patton T. C., A. Ehrlich, and M. K. Smith, Rubber Age (N.Y.) 86, 639 (1960)].

US Patent No. 3,004,917 describes the composition of engine lubricating oils, containing rust inhibitor in which polyethylene glycol-bis-(triricinoleate) with a total molecular weight of 2,000 has been used.

According to German Patent No. 1,940,294 (ClC08f), a polyester of molecular weight 1700 was prepared by autocondensation of 12-hydroxystearic acid condensed with glycidyl methyl acrylate, to introduce unsaturation, and copolymerised with methyl methacrylate. These polymers have been found to increase the stability of non-aqueous polymer dispersions.

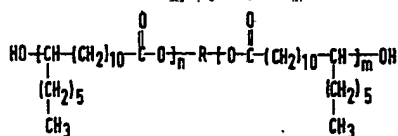
German Patent No. 2,032,297 describes a hydroxyl terminated polyester produced by reacting diol or triol with poly(ω -hydroxycaproic acid) or poly(12-hydroxystearic acid) and these polyesters are used as urethane adhesives for polyvinyl chloride. The preparation of the polyesters with terminal polyhydroxy groups starting from 12-

hydroxy stearic acid and their use as film forming coatings are described in US Patent No. 3,741,941.

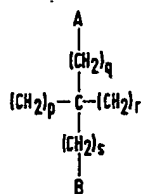
However, none of the above patents covers the concept that is covered in the present invention that provides for a range of polyols for a variety of applications. The present invention, which adopts a method permitting use of the esters of fatty acids of castor oil for production of polyols, can produce ester polyols of average molecular weights ranging from 1500—3200 and functionality in the range of 2 to 4 and of any desired nature of functionality (viz. primary or secondary hydroxyl group) so as to represent a substitute for polyether based polyols, which are petrochemical based.

According to this invention, there is provided a process for the production of an ester-type polyol in which poly-(12-hydroxystearic acid) whereof the degree of polymerization is an integer from 2 to 10 is esterified with a polyol.

By this method one can make, among others, polyols having the formula:



in which n and m, which may be the same or different, are integers from 2 to 10 and R is a group having the formula:

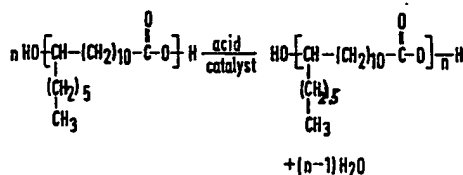


in which p, q, r and s are 0 or integers from 1 to 5; and A and B are H or OH, such that when both q and s are 0, A, B or both A and B must be H.

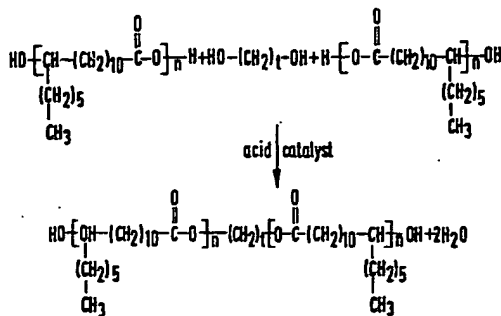
Preferably the poly-(12-hydroxystearic acid) (poly-THSA) is prepared in the first instance by polymerising 12-hydroxystearic acid (THSA) in a solvent in the presence of a catalyst. The catalyst will normally be an acid catalyst and preferably is anhydrous para-toluene sulfonic acid, PTSA. The catalyst is conveniently removed from the reaction product by percolating the reaction mixture through an ion-exchange resin.

Suitable esterifying polyols include glycols, glycerol, tri-methylolpropane and pentaerythritol. Taking a diol as the esterifying polyol, the chemical reactions taking place in the preferred two-step process are given below, wherein 'n' denotes the degree of polymerisation of (12-hydroxystearic acid), the value of which may vary from 2 to 10 and wherein for ethylene glycol 'r' is 2:—

Step 1—Polymerisation



Step 2—Esterification



In the process, water formed during condensation-polymerisation of 12-hydroxy stearic acid can be removed continuously by azeotropic distillation using a solvent (either aliphatic, cyclic or aromatic hydrocarbon) as entraining agent. Bawn *et. al* (Bawn. C. E. H., and Huglin M. B. (Uni Liverpool Engl.), Polymer 3, 257-62 (1962)) found that the degree of polymerisation (DP) in melt polymerisation of THSA at a given temperature is proportional to the concentration of catalyst p-toluene sulphonic acid (PTSA). At a given temperature and concentration of the catalyst, the degree of polymerisation (DP) is found to increase linearly with time. Departure from this phenomenon is found to occur only at higher temperatures (above 150°C). In the present process, polymerisation reaction temperature can be kept under control with the use of suitable solvent as entrainer.

As a first step, THSA is preferably dissolved in an aromatic solvent such as toluene or xylene (to get 20 to 80% solution). THSA is polymerised in solution in the presence of the catalyst PTSA (0.1 to 2% of THSA) to the desired level (DP 2 to 10). The degree of polymerisation is monitored by noting down the drop in acid value of the polymer (poly-THSA), though as an alternative the DP can be determined by measuring the water produced during the reaction. At this stage (DP at desired level), as a preferred second step, a low molecular weight polyol such as glycol, glycerol, trimethylolpropane or pentaerythritol is added to the product of Step-1 so as to react completely with the carboxyl content of poly-THSA. The reaction is continued further till the residual carboxyl groups of poly-THSA are reacted completely to get the desired polyol. The reaction products of Step-2 are percolated through a column of suitable ion-exchange resin where the catalyst, PTSA, is held back after exchange in the column. The entrainer toluene (or xylene) is recovered by distillation, leaving a liquid ester-type polyol behind.

The nature of the hydroxyl groups (such as primary or secondary) in the final product ester-type polyol, the molecular weight of the product and the number of hydroxyl groups required per molecule of product can be controlled in Step-2, as desired, by following the procedure given in the present invention.

The following examples illustrate the typical methods of preparation of different molecular weight polyols modified by diethylene glycol (for poly-diol 1600 to 2000, 2200 to 2600 and 2800 to 3200 molecular weights), 1,1,1-trimethylol-propane (for poly-triols of 2200 to 2600 molecular weight with primary and secondary hydroxyl groups), glycerol (for poly-triols of 2100 to 2700 molecular weights having only secondary hydroxyl groups), pentaerythritol (for poly-tetrols of 2000 to 2500 molecular weight).

Example 1

Preparation of poly-diol of 2200 to 2600 molecular weight range

The experiment was carried out in four stages a, b, c and d as described below:—

- a) 300 g of THSA (minimum 98% purity), 225 ml of distilled commercial toluene and 3 g of anhydrous p-toluene sulphonic acid were charged into a three necked round bottomed (one litre) flask with an arrangement for heating to 120° to 150°C and continuous removal of water azeotropically (Dean and Stark trap). The reaction mixture was kept under agitation by a mercury seal stirrer, fitted to the flask. The water formed by condensation was continuously removed from the system till 13.3 g of water was collected in the Dean and Stark trap (or till the acid value of the reaction products dropped to 30.3 mg KOH/g).
- b) 13.25 g of freshly distilled diethylene glycol was added to the reaction product of (a) immediately after 13.3 g of water was collected. The reaction was further continued till an additional 4.5 g of water was collected and the acid value dropped to 2.3 mg KOH/g.
- c) The reaction mixture was cooled to room temperature and was percolated through a 100 ml column of ion-exchange resin (Zeocarb-225 'Zeocarb' is a registered trade mark) with a free volume of one litre. The percolation rate was maintained at 20 ml. per hour.
- d) The elute obtained after the percolation from (c) was taken in a 1 litre round bottom flask and was distilled under reduced pressure to recover the toluene and 265 g of poly-diol having the following properties:

1. Hydroxyl value (mg KOH/g)	47.5
2. Acid value (mg KOH/g)	1.32
3. Iodine value	1.07
4. Viscosity at 30°C in cps	2100
5. Specific gravity at 27°C	0.926
6. Average molecular weight	2250

Example 2

Preparation of poly-diol of 1600 to 2000 molecular weight range

- 5 a) The procedure followed was same as given in (a) of Example 1, except that the water formed by condensation was continuously removed from the system till 11.74 g of water was collected in the Dean and Stark trap (or till the acid value of the reaction products dropped to 40.54 mg KOH/g).
- 10 b) 17.6 of freshly distilled diethylene glycol was added to the reaction product of (a) immediately after 11.74 g of water was collected and the reaction was further carried out till an additional 6.45 g of water was collected and the acid value dropped to 2.25 mg KOH/g.
- 15 c) The reaction mixture was cooled to room temperature and was percolated through a 100 ml column of ion-exchange resin (Zeocarb-225) with a free volume of one litre. The percolation rate was maintained at 20 ml per hour.
- d) The elute obtained after the percolation from (c) was taken in a 1 litre round bottom flask and was distilled under reduced pressure to recover the toluene and 259 g of poly-diol, having the following properties:

	1. Hydroxyl value (mg KOH/g)	71.0	
	2. Acid value (mg KOH/g)	0.89	
	3. Iodine value	0.98	
20	4. Viscosity at 30°C in cps	2400	20
	5. Specific gravity at 27°C	0.929	
	6. Average molecular weight	1690	

Example 3

Preparation of poly-diol of 2800 to 3200 molecular weight range

- 25 a) The procedure followed was same as given in (a) of Example 1, except that the water formed by condensation was continuously removed from the system till 14.32 g of water was collected in the Dean and Stark trap (till the acid value of the reaction products dropped to 23.83 mg KOH/g).
- 30 b) 10.28 g of freshly distilled diethylene glycol was added to the reaction product of (a) immediately after 14.32 g of water was collected and the reaction was further continued till an additional 3.74 g of water was collected and acid value dropped to 2.79 mg KOH/g.
- 35 c) The reaction mixture was cooled to room temperature and was percolated through a 100 ml column of ion-exchange resin (Zeocarb-225) with a free volume of one litre. The percolation rate was maintained at 20 ml per hour.
- d) The elute obtained after the percolation from (c) was taken in a 1 litre round bottom flask and was distilled under reduced pressure to recover the toluene and 250 g of poly-diol having the following properties: —

	1. Hydroxyl value (mg KOH/g)	32.3	
40	2. Acid value (mg KOH/g)	1.2	40
	3. Iodine value	1.8	
	4. Viscosity at 30°C in Cps	2700	
	5. Specific gravity at 27°C	0.920	
	6. Average molecular weight	2820	

Example 4

Preparation of poly-triol of 2200 to 2600 molecular weight range with primary and secondary hydroxyl groups

- 45 a) The procedure followed was same as given in (a) of Example 1, except that the water formed by condensation was continuously removed from the system till 13.3 g of water was collected in the Dean and Stark trap (or till the acid value of the reaction products dropped to 30.43 mg KOH/g).
- 50 b) 16.32 g of 1,1,1-trimethylol-propane (TMP: poly-THSA: : 1:2) was added to reaction product of (a) after 13.3 g of water was collected, and after cooling down the reaction mix to facilitate the addition of the trimethylol-propane. The reaction was further continued till an additional 4.95 g of water was collected and acid value dropped to 2.15 mg KOH/g.
- 55 c) The reaction mixture was cooled to room temperature and was percolated through a 100 ml column of ion-exchange resin (Zeocarb-225) with a free volume of one litre. The percolation rate was maintained at 20 ml per hour.

- d) The elute obtained after the percolation from (c) was taken in a 1 litre round bottom flask and was distilled under reduced pressure to recover the toluene and 260 g of poly-triol having the following properties:

1. Hydroxyl value (mg KOH/g)	63
2. Acid value (mg KOH/g)	0.5
3. Iodine value	0.81
4. Viscosity at 30°C in cps	2100
5. Specific Gravity at 27°C	0.932
6. Average molecular weight	2260

10

Example 5

10

Preparation of poly-triol of 2100 to 2700 molecular weight range with only secondary hydroxyl groups

15

- a) The procedure followed was same as given in (a) of Example 1, except that the water formed by condensation was continuously removed from the system till 13.41 g of water was collected in the Dean and Stark trap (or till the acid value of the reaction products dropped to 29.97 mg KOH/g).
- b) 11.2 g of glycerine (minimum purity 99%) was added to the reaction product of (a) immediately after 13.41 g. of water was collected and the reaction was further continued till an additional 4.90 g of water was collected and acid value dropped to 3.05 mg KOH/g.
- c) The reaction mixture was cooled to room temperature and was percolated through a 100 ml column of ion-exchange resin (Zeocarb-225) with a free volume of one litre. The percolation rate was maintained at 20 ml per hour.
- d) The elute obtained after the percolation from (c) was taken in a 1 litre round bottom flask and was distilled under reduced pressure to recover the toluene and 255 g of poly-triol having the following properties:

15

20

20

25

25

1. Hydroxyl value (mg KOH/g)	53.00
2. Acid value (mg KOH/g)	3.0
3. Iodine value	0.98
4. Viscosity at 30°C in cps	1800
5. Specific gravity at 27°C	0.925
6. Average Molecular weight	2350

30

30

Example 6

Preparation of poly-tetrol of 2000 to 2500 molecular weight range

35

35

- a) The procedure followed was same as given in (a) of Example 1, except that 210 ml of xylene was taken in place of toluene and that the water formed by condensation was continuously removed from the system till 13.42 g of water was collected in the Dean and Stark trap (or till the acid value of the reaction products dropped to 30.15 mg KOH/g).
- b) 17.82 g of pentaerythritol was added to the reaction product of (a) immediately after 13.42 g of water was collected and the reaction was further continued till an additional 4.95 g of water was collected and acid value dropped to 2.95 mg KOH/g.
- c) The reaction mixture was cooled to room temperature and was percolated through a 100 ml column of ion-exchange resin (Zeocarb-225) with a free column of 1 litre. The percolation rate was maintained at 20 ml per hour.
- d) The elute obtained after the percolation from (c) was taken in a 1 litre round bottom flask and was distilled under reduced pressure to recover the xylene and 263 g of poly-tetrol having the following properties:

40

40

45

45

50

50

1. Hydroxyl value (mg KOH/g)	82
2. Acid value (mg KOH/g)	1.8
3. Iodine value	2.4
4. Viscosity at 30°C in cps	2050
5. Specific gravity at 27°C	0.937
6. Average molecular weight	2050

55

55

WHAT WE CLAIM IS:—

1. A process for the production of an ester-type polyol in which poly-(12-hydroxystearic acid) whereof the degree of polymerisation is an integer from 2 to 10 is esterified with a polyol.

2. A process according to Claim 1 in which said esterifying polyol is a glycol, glycerol, trimethylol-propane or pentaerythritol.

3. A process according to Claim 1 or Claim 2, in which the poly-(12-hydroxystearic acid) is first prepared by polymerizing 12-hydroxystearic acid in a solvent in the presence of a catalyst.

4. A process according to Claim 3 in which said solvent is an aromatic solvent.

5. A process according to Claim 4 in which said aromatic solvent is toluene or xylene.

6. A process according to any of Claims 3 to 5 in which said catalyst is *p*-toluene sulphonic acid.

7. A process according to any of Claims 3 to 8 in which said esterifying polyol is added to said 12-hydroxystearic acid during polymerization when the degree of polymerization of said 12-hydroxystearic acid is an integer from 2 to 10.

8. A process according to Claim 7 in which said degree of polymerization is determined by measuring the acid value of the polymerizing 12-hydroxystearic acid.

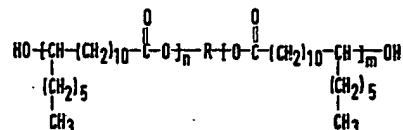
9. A process according to Claim 7 in which said degree of polymerization is determined by measuring the amount of water produced in the polymerization reaction.

10. A process according to any of Claims 3 to 9 in which said catalyst is removed after the esterification of said poly-(12-hydroxystearic acid) by passing the reaction mixture through an ion-exchange resin.

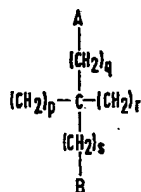
11. A process according to Claim 1, substantially as herein described with reference to any one of the foregoing Examples.

12. An ester-type polyol when produced by a process according to any one of the preceding Claims.

13. A polyol having the formula:



in which *n* and *m*, which may be the same or different, are integers from 2 to 10 and *R* is a group having the formula:



in which *p*, *q*, *r* and *s* are 0 or integers from 1 to 5; and *A* and *B* are H or OH, such that when both *q* and *s* are 0, *A*, *B* or both *A* and *B* must be H.

MARKS & CLERK,
Chartered Patent Agents,
57-60 Lincoln's Inn Fields,
London, WC2A 3LS.
Agents for the Applicant(s).

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1978
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

Brown, Cecelia

From: Austin, Javii Davis
Sent: Monday, October 01, 2007 11:49 AM
To: Ahmed, Ali; Brown, Cecelia
Cc: Research Files
Subject: (2 patents) RE: 05725.1540-00000
Attachments: fr618.pdf; gb782.pdf

Ali, I found FR 2792618 on the Patent Fetcher website. Also, IN 143864 is not readily available and could take a few weeks to come in as it was not available through the online databases and needs to be special ordered. I checked Espacenet and found its English counterpart - GB 1524782. The fulltext was available for free so I downloaded it and have attached it along with the French patent. Please let me know if you are still interested in the original Indian publication. -Javii

From: Ahmed, Ali
Sent: Monday, October 01, 2007 9:35 AM
To: Austin, Javii Davis; Brown, Cecelia
Cc: Research Files
Subject: RE: (15 patents) RE: 05725.1540-00000

Thanks Javii. In the future, please use patentfetcher.com as its free and even easier to use than MicroPatent. We still get the same quality PDF's through patentfetcher and its free ;)

Please give me a call regarding the Derwent Abstracts when you have a chance.

Thanks
Ali

From: Austin, Javii Davis
Sent: Monday, October 01, 2007 9:23 AM
To: Ahmed, Ali; Brown, Cecelia
Cc: Research Files
Subject: RE: (15 patents) RE: 05725.1540-00000

Ali, I'll check on this in the future. I accessed the majority of the patents through MicroPatent. The cost for US, EP, and WO patents is \$3.95 per document and for other foreign patents is \$7.95 per patent. The total charges for the patents was \$99.30. 2 patents were not available through MicroPatent and have been requested through a patent service. If you have any other questions or concerns regarding the costs please let me know. Thanks, Javii

Javii D. Austin
Research Librarian
tele. 202-408-4373